

# Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops<sup>†</sup>

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Bio-oils from the fast pyrolysis of switchgrass forage and two sets of alfalfa stems (from two stages of development—bud and full flower stages) have been analyzed by wet-chemical methods, GC-MS, and HPLC. The chemical composition of bio-oil is important because it may give insights into its quality, stability, or suitability for downstream upgrading. Pyrolysis experiments were conducted at 500 °C under a nitrogen atmosphere in 2.5 kg/h fluidized bed reactor. A total of 62 chemical species were positively identified in the liquids. Of the identified compounds, 27 have been quantified. The chemical compositions of the bio-oils are compared with what is known about the compositions of these feedstocks. While the compositions of the bio-oil from the two alfalfa stems were similar, there were numerous differences in the compositions of the alfalfa and switchgrass bio-oils. Noted are the higher levels of nitrogen, water, and aromatic hydrocarbons in bio-oils produced from alfalfa stems than from switchgrass and woody feedstocks that have been previously characterized. Also noted is a much lower concentration of levoglucosan and hydroxyacetaldehyde concentrations among bio-oils from alfalfa stems compared with bio-oil from switchgrass or woody biomass.

## Introduction

Because it offers numerous advantages over biochemical-based transformation methods, thermochemical conversion of lignocellulosic biomass (i.e., combustion, pyrolysis, or gasification) is receiving increasing interest and utility as a method for production of renewable energy and fuels.<sup>1</sup> Fast pyrolysis, a rapid decomposition of organic matter in the absence of oxygen, produces solid (char), liquid (pyrolysis oil or pyrolysis liquid; bio-oil when produced from biomass), and gas (or noncondensable gas, NCG) with the liquid comprising the largest product fraction when pyrolysis is conducted at 500 °C. Fast pyrolysis of lignocellulosic biomass results in extensive depolymerization and fragmentation of the biopolymers (cellulose, hemicellulose, and lignin) of which it is composed. Direct combustion of bio-oils as a substitute for heavy-fuel oil in boilers and gas turbines has been demonstrated.<sup>2</sup> For bio-oil to be refined into usable transportation fuel, post-production upgrading to decrease its oxygen content is required.<sup>3</sup>

Boateng et al.<sup>4</sup> have developed a bench-scale fluidized bed reactor fast pyrolyzer to study bio-oil production from agricultural residues including potential energy crops being developed within the Agricultural Research Service (ARS) of the U.S. Department of Agriculture (USDA). Thus far, bio-oil has been produced from two potential energy crops, switchgrass<sup>4</sup> and

Table 1. Analysis of Biomass Samples Used for Pyrolysis

	switchgrass <sup>a</sup>	alfalfa-early bud	alfalfa-full flower
proximate (wt %, db)			
volatile matter	83.41	73.39	75.29
ash	2.61	8.74	5.83
fixed carbon	13.98	17.87	18.88
ultimate (wt %, db)			
C	47.53	44.30	45.97
H	6.81	5.43	5.52
N	0.51	2.52	1.60
S	0.00	0.22	0.088
Cl	— <sup>b</sup>	0.59	0.41
O	42.54	38.20	40.58

<sup>a</sup> Taken from Boateng et al.<sup>4</sup> <sup>b</sup> Cl content not determined for switchgrass.

alfalfa stems.<sup>5</sup> Switchgrass and alfalfa both have great potential as energy crops because both species are perennial crops that do not require annual reseeding and require lower agricultural inputs (fertilizer and pesticides).<sup>6</sup> Boateng et al. have previously studied the pyrolysis of each of these feedstocks on an analytical scale with a pyrolysis probe coupled with a GC-MS (py-GC-MS) but only a qualitative measure of the pyrolysis oils was possible.<sup>7,8</sup>

There are significant problems with bio-oil from fast pyrolysis that currently limit its use as a fuel. Due to its much higher oxygen content, the average bio-oil has energy content about half of that crude oil. It is also plagued by poor volatility, high viscosity, and corrosiveness.<sup>2,9</sup> Raw bio-oil

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<sup>†</sup> Disclaimer: Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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**Table 2. Chemical Composition (g kg<sup>-1</sup>, db) of Switchgrass and Alfalfa Stems Used in Pyrolysis Study**

	cellulose	hemicellulose	lignin	crude protein
switchgrass <sup>a</sup>	321	284	163	
alfalfa, early bud <sup>b</sup>	275	205	158	127
alfalfa, full flower <sup>b</sup>	306	217	175	88

<sup>a</sup> Adapted from Alder et al.<sup>13</sup> <sup>b</sup> Adapted from Dien et al.<sup>6</sup>

**Table 3. Elemental Analysis of Bio-Oil**

wt %, db	switchgrass	alfalfa, early bud	alfalfa, full flower
C	47.47	53.88	56.84
H	6.96	8.47	7.86
N	0.36	4.59	3.73
S	— <sup>a</sup>	0.05	0.07
Cl (ppm)	— <sup>a</sup>	249	242
O	45.19	32.73	31.30
ash	0.01	0.28	0.30

<sup>a</sup> S and Cl content not determined for bio-oil derived from switchgrass.

can contain between 10 and 30 wt % water and hundreds of various oxygenated organic compounds. Some of these components are highly reactive and can cause pyrolysis oil to be unstable, resulting in higher water content and an increase in viscosity over time.<sup>2,9</sup>

The chemical composition, and therefore the properties mentioned above, of bio-oil depends on the feedstock, pyrolysis conditions, and product collection methods. Additionally, post-production processing success will vary with bio-oil composition. Therefore, compositional data on bio-oils is needed to identify the feedstocks and pyrolysis conditions which are optimal for high-quality bio-oil production. Herein, the chemical compositions of bio-oils produced from the above-mentioned energy crops via GC/MS and HPLC analysis are reported.

### Experimental Section

**Biomass.** The switchgrass forage samples were of the Cave-in-Rock variety and were provided from ARS's Pasture Systems and Watershed Management Unit at University Park, PA. The switchgrass was harvested at a 10 cm stubble height from plots in Rock Springs, PA. The alfalfa stem samples utilized were collected from 2 year old stands at Becker and Rosemount, MN, at two stages of maturity. Alfalfa was harvested when it had reached the bud (unopened flower buds present) and at full flower (open flowers on all stems) stages of development. Feedstocks were ground in a Wiley mill using a 2 mm screen and dried for 24 h at 80 °C prior to use.

**Pyrolysis.** Pyrolysis was carried out on a bench-scale fluidized bed pyrolyzer. The complete reactor design has been previously reported.<sup>4</sup> Briefly, the biomass feed system consisted of a 30 L capacity metering hopper and a twin-screw auger feed delivery

system. The reactor vessel consisted of a vertical stainless steel pipe, with a 7.8 cm diameter and 52 cm height. The fluidized medium was silica sand with a nominal diameter of 850 μm. Preheated nitrogen was used as the fluidization gas, added through a mass flow controller at 105 L/min. The reactor was heated by two clamshell type heaters. Pyrolysis was conducted at a reactor temperature of ~500 °C. Char was collected by two cyclone separators mounted in series; this served as the main gas cleanup system that removed the solids from the gas stream prior to condensation. Bio-oil was collected via a series of four canisters cooled in water/dry ice bath followed by an electrostatic precipitator (ESP). The fraction of oil collected was consistently highest at the ESP (40–60% of liquid product). Additionally, this fraction of oil was the highest quality (based on low water content and homogeneity) of any of bio-oil fractions collected. Results in this paper reflect the whole bio-oil. Overall yields of bio-oil were 60% for switchgrass, and 45% and 53% for early bud and full flower alfalfa stems respectively. The high heating values of the oils were 18 445, 25 852, and 26 542 for switchgrass, early bud alfalfa, and full flower alfalfa, respectively.

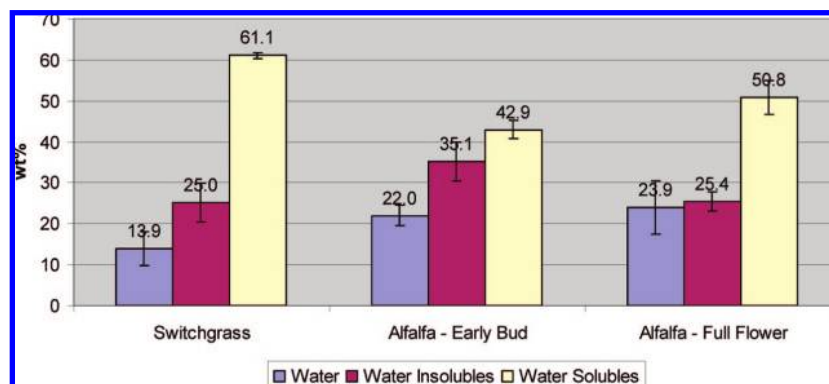
**Analysis.** Water content of the bio-oils were determined by Karl Fischer (KF) titration using 3:1 methanol:chloroform as solvent. Water insolubles (consisting of pyrolytic lignin and extractives) were determined by mixing warm water and bio-oil in a 2:1 ratio, filtration of the sample through a 0.45 μm PTFE filter followed by determining the water content of the aqueous layer by KF. Water insolubles (WIS) were then calculated by following equation:<sup>10</sup>

$$\% \text{WIS} = \{[A - (B + C) \times 100]/D\} - (B + C)/A \times 100$$

where *A* is weight dry oil (g), *B* water content in oil (g), *C* water added (g), and *D* water content by KF after water addition and filtration; water solubles were then determined by difference.

GC/MS analysis of bio-oil was performed on an Agilent 6890N GC equipped with an Agilent 5973 mass-selective detector (MSD). The GC column used was a DB-1701 60m × 0.25 mm, 0.25 μm film thickness. The oven was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C, and hold there for 20 min. The injector temperature was 250 °C, and the injector split ratio was set to 30:1. The flow rate was 1 mL/min of the He carrier gas. The bio-oil samples were prepared as ~6% solutions in acetone which were filtered through a 0.45 μm PTFE filter prior to injection. For quantification of components, relative response factors were determined relative to the internal standard, fluoroanthene.<sup>11</sup>

HPLC analysis of the bio-oils was performed on a Waters Breeze HPLC system using a refractive index detector, set at 30 °C. The column used was an Aminex HPX-87H, 300 × 7.8 mm (Bio-Rad, Inc.), and was heated to 30 °C. The mobile phase was 0.007 N H<sub>3</sub>PO<sub>4</sub>. The pump was programmed at a flow rate 0.6 mL/min and *n*-propanol was used as the internal standard for quantification.<sup>11</sup>

**Figure 1.** Bio-oil solubility profile.

**Table 4. Compounds Detected in Pyrolysis oil from Switchgrass and Alfalfa<sup>a</sup>**

compound	group	switchgrass	alfalfa, early bud	alfalfa, full flower
acetic acid	acid	X	X	X
propionic acid	acid	X	X	X
ethylene glycol	alcohol	X	X	X
hydroquinone	alcohol	X	X	X
glyoxal	aldehyde	X	X	X
tetradecene	alkene	X		
benzene	aromatic			X
toluene	aromatic		X	X
styrene	aromatic		X	X
indene	aromatic		X	X
methylindene	aromatic		X	X
naphthalene	aromatic		X	X
methyl-naphthalene	aromatic	X	X	X
butyrolactone	ester	X	X	X
furfural	furan	X		
furfuryl alcohol	furan		X	X
1-(2-furyl)ethanone	furan	X	X	X
4-methyl-3-penten-2-one	ketone		X	
2-cyclopenten-1-one	ketone		X	X
2-methyl-2-cyclopenten-1-one	ketone	X	X	X
2,3-dimethyl-2-cyclopenten-1-one	ketone	X	X	X
3-methyl-2-cyclopenten-1-one	ketone	X	X	X
3,4-dimethyl-2-cyclopenten-1-one	ketone	X	X	X
2-hydroxy-3-methyl-2-cyclopenten-1-one	ketone	X	X	X
3-ethyl-2-cyclopenten-1-one	ketone	X	X	X
3-ethyl-2-hydroxy-2-cyclopenten-1-one	ketone	X	X	X
2,3-dihydroxy-1H-inden-1-one	ketone	X	X	X
2,2,6,6-tetramethylpiperidone	nitrogen		X	X
benzyl nitrile	nitrogen	X	X	X
pyridinol	nitrogen		X	X
indole	nitrogen		X	X
methylindole	nitrogen		X	X
hydroxyacetaldehyde	oxygenate	X		
acetol	oxygenate	X	X	X
1-hydroxy-2-butanone	oxygenate			X
4-hydroxy-4-methyl-2-pentanone	oxygenate		X	X
1-ethyl-4-methoxybenzene	oxygenate			X
2,3-dihydrobenzofuran	oxygenate		X	X
guaiacol	phenol	X	X	X
2-methoxy-4-methylphenol	phenol	X	X	X
4-ethyl-2-methoxyphenol	phenol	X		X
2-methoxy-4-vinylphenol	phenol	X		
eugenol	phenol	X		
isoeugenol	phenol	X	X	X
2,6-dimethoxyphenol	phenol	X	X	X
phenol	phenol	X	X	X
<i>o</i> -cresol	phenol	X	X	X
2,5-dimethylphenol	phenol	X	X	X
<i>p</i> -cresol	phenol	X	X	X
<i>m</i> -cresol	phenol	X	X	X
2,4-dimethylphenol	phenol	X	X	X
3,5-dimethylphenol	phenol	X	X	X
4-ethyl phenol	phenol	X	X	X
3-ethylphenol	phenol	X	X	X
2-ethylphenol	phenol	X	X	X
4-ethyl-3-methyl phenol	phenol	X	X	X
4-(1-methylethyl)phenol	phenol	X		X
2-me-1,4-benzenediol	phenol	X	X	X
2,3-anhydro-D-mannosan	sugar	X		
1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose	sugar	X	X	X
levoglucosan	sugar	X	X	X

<sup>a</sup> X = detected.

Proximate and ultimate analysis on biomass and bio-oil was performed by Galbraith Laboratories, Inc. (Knoxville, TN).

## Results and Discussion

**Biomass Composition.** Physical and elemental analysis of the biomass used for these studies is presented in Table 1. Major differences can be seen between the types of biomass. The ash content of the biomass samples is much higher for both of the alfalfa stems than it is for the switchgrass, and ash content is higher for the less mature alfalfa stems. This is significant because alkali metals contained in the ash have been shown to be catalysts for changing the depolymerization mechanisms during pyrolysis leading to changes in the composition of pyrolysis products.<sup>12</sup> The percentage of fixed carbon is also greater in the alfalfa stems than in the switchgrass samples, resulting in the switchgrass containing >10% more volatile matter than the alfalfa stems. The elemental analysis reveals that the nitrogen content is much greater for the alfalfa stems than for switchgrass as would be expected because alfalfa is a nitrogen fixing legume. The nitrogen levels were higher in the alfalfa stems at the early bud stage.

Further characterization of the cellulose, hemicellulose, and lignin polymers in the cell walls of the switchgrass and alfalfa stem biomass has been done by Adler et al.<sup>13</sup> and Dien et al.,<sup>6</sup> respectively. The concentrations of these polymers and protein in the biomass used in this study are presented in Table 2. The levels of cellulose and hemicellulose are greater for the switchgrass than the alfalfa stems. The amount of each of the polymers in alfalfa stems increases as the plant matures, and the cellulose/hemicellulose to lignin ratio remains at 3.0:1. That ratio for the switchgrass sample is 3.7:1. Protein levels decrease in the alfalfa stems as the plant matures; this data was not available for the switchgrass but judging from the nitrogen levels in the elemental analysis its protein levels should be below those of the alfalfa stems.

**Bio-oil Composition.** Analysis of the bio-oil product from pyrolysis of switchgrass and alfalfa stems is presented as a whole oil, the sum of all the bio-oil fractions collected from the four condenser canisters and from the ESP. The elemental analysis of the bio-oil on a dry basis is presented in Table 3. The elemental composition of the bio-oil from switchgrass mirrors that of the biomass (Table 1). However, bio-oil from both samples of alfalfa stems has a higher percentage of carbon and lower percentage of oxygen when compared with both the alfalfa biomass and the switchgrass bio-oil. A possible reason for this difference is that more oxygen content is found in the noncondensable gas (CO<sub>2</sub> constitutes ~60% of NCG from alfalfa stems and ~30% from switchgrass)<sup>4,5</sup> and the larger amounts reaction water for alfalfa stems than for switchgrass. Differences in the water content of bio-oils are a result of variation in the water produced as a pyrolysis product, as all the biomass samples were dried to about 5% moisture content prior to use. Water content of the bio-oils from switchgrass was 13.91%, 21.96%

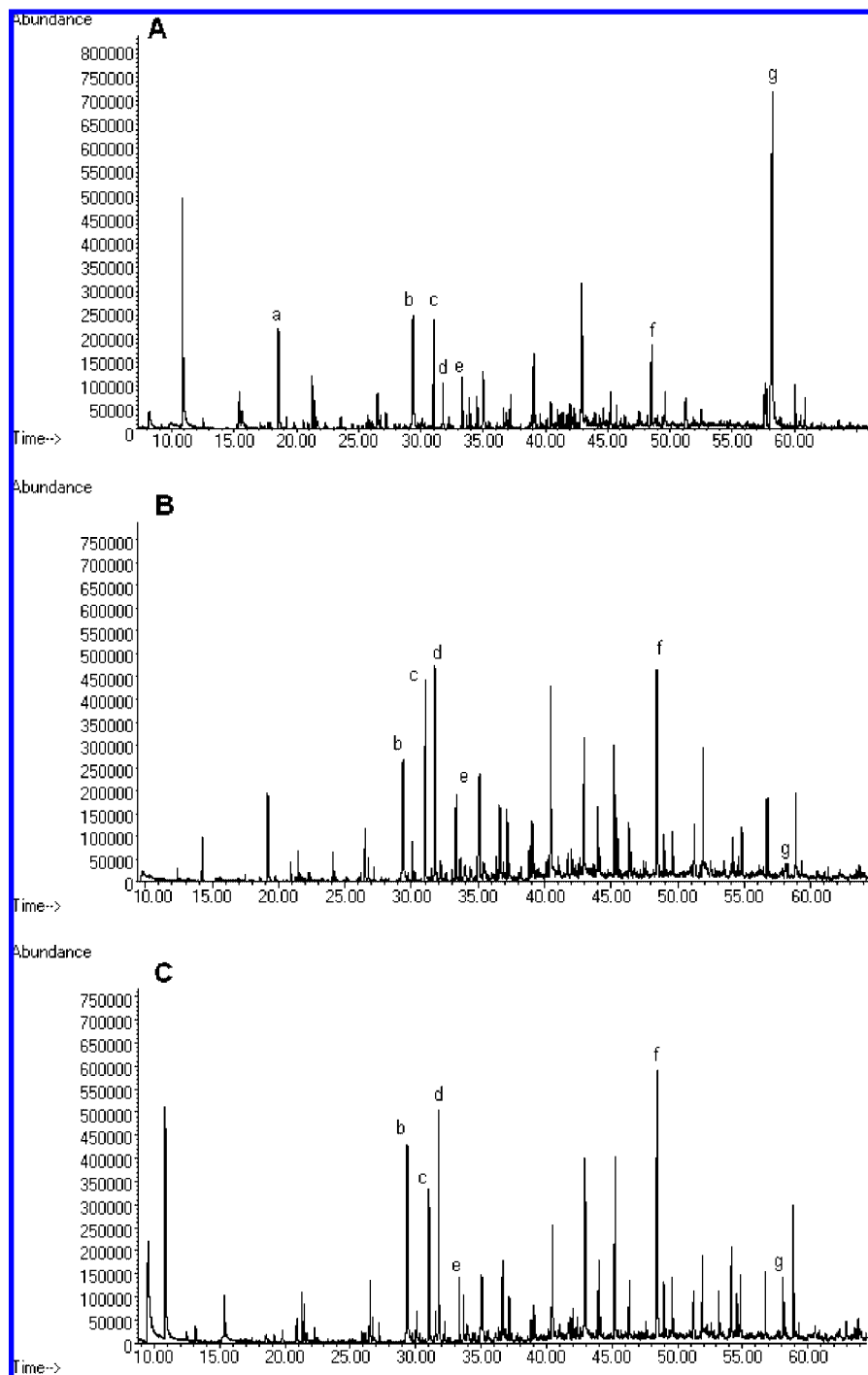
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**Figure 2.** Total ion chromatograms for bio-oil from (A) switchgrass forage, (B) early bud alfalfa stems, and (C) full flower alfalfa stems. Labeled peaks are (a) furfural, (b) 2-hydroxy-3-methyl-2-cyclopenten-1-one, (c) phenol, (d) guaiacol, (e) cresols, (f) isoeugenol, and (g) levoglucosan.

from early bud alfalfa, and 23.86% from full flower alfalfa. Water-insoluble compounds made up about 25–35% of the total oil for all of the bio-oils produced (Figure 1). The water-insoluble fraction consists mainly of pyrolytic lignin (higher molecular weight oligomers of partially depolymerized lignin) and extractives (defined as hexane-soluble compounds). Extractives were more prevalent in bio-oil from alfalfa stems than from switchgrass; more water-insoluble black sticky material was observed to precipitate with pyrolytic lignin in the case of alfalfa bio-oil and more aromatic hydrocarbons were detected by GC-MS (*vide infra*) for alfalfa bio-oil. Water-soluble compounds include acids, alcohols, aldehydes, ketones, and sugars.<sup>3,9</sup> A large amount of the water solubles is mainly derived from the decomposition of cellulose and hemicellulose,<sup>3</sup> and

the higher levels of those constituents in the switchgrass biomass versus the alfalfa stems is reflected in the compositions of the bio-oil.

Individual chemical compounds contained in the bio-oils from pyrolysis of these energy crops were identified by GC-MS and HPLC (Table 4, Figure 2). Quantitative concentrations of some these compounds are found in Table 5. Qualitative differences observed between the bio-oil from the three different biomass feedstocks include the observations of more oxygen-free aromatic hydrocarbons in the alfalfa stems derived bio-oils than in the switchgrass bio-oil. Aromatic hydrocarbons detected in the alfalfa stem bio-oils are benzene, toluene, indene, methylindene, naphthalene, and methylnaphthalene; of these only methylnaphthalene was observed in the switchgrass bio-oil.



Table 5. Quantification of Some Bio-oil Components (wt %)

quantification method	compound	group	switchgrass	alfalfa, early bud	alfalfa, full flower	typical wood <sup>a</sup>
Cellulose/Hemicellulose-Derived Compounds (wt %)						
HPLC	acetic acid	acids	2.94	2.26	3.49	0.5–12
HPLC	glyoxal	aldehyde	trace	0.35	1.05	
GC	furfural	furan	0.62			0.1–1.1
GC	furfuryl alcohol	furan		0.18	0.20	0.1–5.2
GC	2-methyl-2-cyclopenten-1-one	ketone	0.16	0.27	0.26	
GC	3-methyl-2-cyclopenten-1-one	ketone	0.34	0.46	0.44	
HPLC	hydroxyacetaldehyde	oxygenates	2.40			0.9–13
GC	4-hydroxy-4-methyl-2-pentanone	oxygenates	0.05	0.24	0.04	
HPLC	acetol	oxygenates	2.75	0.78	2.35	0.7–7.4
HPLC	levoglucosan	sugar	6.38	0.14	0.37	4.8–5.4
Lignin-Derived Compounds (wt %)						
GC	guaiacol	phenol	0.18	0.51	0.46	0.1–1.1
GC	2-methoxy-4-methylphenol	phenol	0.07	0.21	0.16	0.1–1.9
GC	isoeugenol	phenol	0.45	0.70	0.73	0.1–7.2
GC	2,6-dimethoxyphenol	phenol	0.20	0.37	0.43	0.7–4.8
GC	phenol	phenol	0.66	1.14	0.95	0.1–3.8
GC	<i>o</i> -cresol	phenol	0.19	0.30	0.24	0.1–0.6
GC	2,5-dimethylphenol	phenol	0.01	0.08	0.07	
GC	<i>p</i> -cresol	phenol	0.27	0.44	0.33	0.1–0.5
GC	<i>m</i> -cresol	phenol	0.20	0.47	0.34	0.1–0.4
GC	2,4-dimethylphenol	phenol	0.10	0.17	0.14	0.1–0.3
GC	3,5-dimethylphenol	phenol	0.05	0.12	0.08	
GC	4-ethylphenol	phenol	0.22	0.17	0.15	
GC	3-ethylphenol	phenol	0.04	0.06	0.06	
GC	2-ethylphenol	phenol	0.03	0.07	0.04	0.1–1.3
Protein-Derived Compounds (wt %)						
GC	benzyl nitrile	nitrogen	trace	0.10	0.06	
GC	indole	nitrogen		0.15	0.01	

<sup>a</sup> From Diebold.<sup>14</sup>

More nitrogen-containing compounds were found in the alfalfa stem bio-oils as well, reflecting the higher nitrogen content of the alfalfa stems biomass versus the switchgrass. Nitrogen-containing compounds found in the alfalfa stems bio-oils are 2,2,6,6-tetramethylpiperidone, benzonitrile, pyridinol, indole, and methylindole. Of these, only benzonitrile was found in switchgrass. The amount of benzonitrile and indole were quantified (Table 5). The level of benzonitrile was too low to be quantified for the switchgrass bio-oil and the alfalfa stems bio-oil contained 0.10 wt % for the early bud variety and 0.06 wt % for the full flower variety. Indole was found in 0.15 wt % for the early bud alfalfa stem bio-oil and 0.01 wt % for the full flower variety. The higher levels of these nitrogen-containing compounds in the early bud alfalfa bio-oil compared with the full flower alfalfa bio-oil reflect the higher nitrogen content of the less mature biomass.

Also among the major differences between the bio-oils from the three biomass feedstocks are the concentrations of the water-soluble materials derived from cellulose and hemicellulose. Levoglucosan, an anhydro sugar, is a major product of cellulose decomposition. In this case, levoglucosan concentration in switchgrass-derived bio-oil (6.4 wt %) was higher than typical values for bio-oils from wood (up to 5.4 wt %),<sup>14</sup> but the levels of levoglucosan from alfalfa stems were lower than typical and much lower than those of switchgrass pyrolysis oil, <0.5 wt %. Alkali metals contained in the ash of biomass have been shown to change the mechanistic pathways of cellulose decomposition to favor formation of hydroxyacetaldehyde over levoglucosan; however, despite the low concentrations of levoglucosan found in the alfalfa stems bio-oils, no hydroxyacetaldehyde was detected in these bio-oils. Bio-oil derived from switchgrass

contained 2.4 wt % hydroxyacetaldehyde, and bio-oil from wood can contain up to 13 wt % hydroxyacetaldehyde.<sup>14</sup> Acetol, another major water-soluble compound found in biomass pyrolysis oils, was found in concentrations of 0.8 wt % for early bud alfalfa derived bio-oil, 2.4 wt % for full flower alfalfa bio-oil and 2.8% for switchgrass bio-oil, all within typical levels found in bio-oil from wood.<sup>14</sup> Acetic acid concentrations were similar for all three bio-oils, varying between 2.25 and 3.50 wt %, again within typical values for bio-oil from wood.<sup>14</sup>

Lignin-derived phenolic compounds found in the bio-oils were detected by GC-MS. In all of the bio-oils from these energy crops, phenol was most abundant compound from lignin with concentration of ~0.7 wt % in switchgrass bio-oil and ~1.0 wt % alfalfa stems. These levels fall within the range of phenol typically found in bio-oils from woody biomass.<sup>14</sup> Other phenolic compounds found in the bio-oils from switchgrass and alfalfa stem bio-oils include guaiacol (2-methoxyphenol), 2,6-dimethoxyphenol, isoeugenol, cresols, dimethylphenols, and ethyl phenols. Generally, the levels of these phenolic compounds were higher for the alfalfa stems than for the switchgrass bio-oils, but within the ranges of levels found for woody biomass.<sup>14</sup>

## Conclusions

The chemical compositions of fast pyrolysis bio-oils from two different potential energy crops, switchgrass and alfalfa stems, have been studied by GC-MS and HPLC analysis. This data is important in evaluating the use of bio-oil from energy crops and for comparing it to pyrolysis products from wood. The alfalfa stems were taken from alfalfa plants harvested at two different stages of maturity. Differences among the bio-oils from these three different biomasses include more aromatic hydrocarbons and nitrogen-containing compounds found in the alfalfa stems derived bio-oils versus the switchgrass bio-oils. Levoglucosan levels were >12× higher in the switchgrass oils

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than the alfalfa stem oils. More water was generated in the pyrolysis of alfalfa stems than in the pyrolysis of switchgrass. Further studies for production of high-quality bio-oil from agricultural feedstocks including various biomasses and process conditions are underway. Understanding the compositions of bio-oils from energy crops will add to their use in thermochemical conversion platforms, as this information will be extremely important in evaluating the bio-oils' stabilities, properties, and toxicities. It will also be useful in identifying

and solving challenges associated with further refining of bio-oils into liquid fuels.

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